ХИМИЯ

BIOSOURCED SILICA/AG COMPOSITE MATERIALS AS A NEW ADSORBENT FOR THE REMOVAL OF MERCURY IONS FROM WATER

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ABSTRACT

In this study, the synthesis of a new composite adsorbent using rice biosourced silica, silver nanoparticles and triethoxysilane as the raw materials for removal aqueous mercury ions from water is presented. The new composite material was synthesised by modification of the surface of rice husk based silica with silane groups and farther decoration with silver nanoparticles. Characterization was carried out through, Fourier transform infrared (FT-IR) spectra analysis, N_2 adsorption-desorption (Brunauer-Emmett-Teller) and thermal gravimetric analysis (TGA). Synthetic and real mercury containing water sampled from Balkyldak lake-reservoir, Kazakhstan were tested. The results demonstrated that the affinity of the composite for mercury is high and the removal mechanism is adsorption accompanied by an amalgamation reaction between silver and mercury.
Key words: Adsorption, silver nanoparticles, rice husk silica, silica/Ag composites, aqueous mercury ions
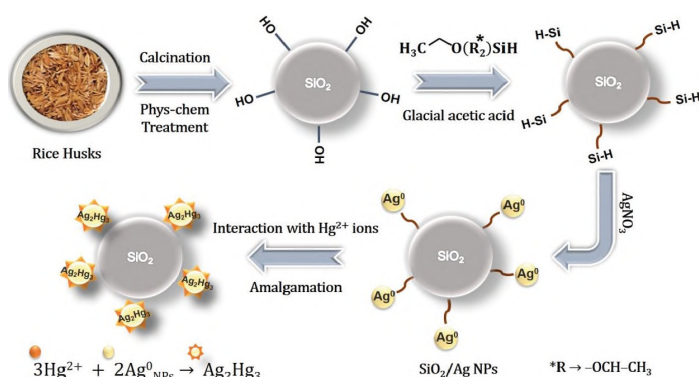
Graphical abstract

Figure 0 – Schematic illustration of the experimental procedure of composite materials fabrication.
The suggested mechanism for adsorption of Hg^{2+} ions on the rice husk based SiO_2/AgNPs composite materials is demonstrated on Fig. 0.

Introduction. Currently water contaminations with heavy metals have great interest. Even at low concentrations, these metals have a toxic affects to environment and microorganisms. Mercury is one of the most harmful pollutants among heavy metals. It is widespread in natural waters, groundwater, draining water in urban areas, and industrial waste [1]. Consequently, development of efficient clean-up technologies for removal of mercury from aqueous media has been required testing various methods such as ion exchange, precipitation, reduction, solvent extraction, reverse osmosis and so on. However, compared to adsorbents all these methods have deficiencies such as high cost, low efficiency, formation of by-products, and unsuccessful at low toxic metal concentrations (1–20 mg·L-1) etc. Hence, many researches have been considered adsorption is the most advantageous technique for elimination Hg^{2+} ions from wastewater [2].

According to United States Environmental Protection Agency (USEPA) the minimum allowable limit of mercury concentration for drinking water is 0.002 mg/l, whereas for World Health Organization this was set at 0.006 mg/l [3]. Besides, mercury discharge into water sources has been increased in Asia, South America, and Africa due to elevated mercury pollution from industrial plants [4].

Kazakhstan is also vulnerable in terms of ecological problems concerning mercury pollution of water resources. The brightest example is the technical reservoir Balkyldak, which is located near the industrial district of Pavlodar city in the north of Kazakhstan. This waterbody was intended to store and evaporate industrial

wastes of several large-scale plants in Pavlodar, among them are the Pavlodar Oil Chemical Refinery (POCR) LLP, the Pavlodar Chemical Plant "Caustic" JSC and the heat electric generation plant [5]. The industrial effluent entering the reservoir contains various pollutants, such as petrochemicals, heavy metal salts (Zn, Fe, Cr, Hg etc.), chlorine, sulphates etc. Recent research conducted by Karaganda State Technical University on monitoring of toxic metal contamination in the northern district of Pavlodar showed that the mercury content in soil and groundwater exceeds allowable limit, which verifies that this region is still remains the main focus of mercury pollution. In addition, mercury discharges into Balkyldak reservoir was greatly enhanced by operation of an industrial object so called ex-"Chimprom", which produced chlorine and sodium through electrolysis with mercury cathode between 1973 and 1992. During 14 years the 1089.36 tons of metallic mercury was consumed. In addition to small discharge of mercury into waterbody during regular plant operations, the significant leakages occurred during the shutdown of the plant. Mercury discharge into aquatic systems of the lake-accumulator Balkyldak has an adverse impact on flora and fauna in this region. The analysis of tench fish, which is inhabitant of the lake, showed that mercury concentration in fish exceeds the allowable minimum limit in 0.53 and 3.73 times. The maximum amount of mercury content was found in perch, which is equal to 5.6 times maximum permissible concentration (MPC) [5]. Furthermore, comparison of water content in the Balkyldak Lake and in groundwater showed that mercury concentration has increased in groundwater, whereas the concentration of zinc and chromium remains unchanged. The major concern relates to the spread of mercury pollution into the Irtysh River, which is one of the largest waterbodies in Kazakhstan. In 1950s, mercury pollution from a chemical plant in Minamata Bay caused contamination of fish, which was the main food supply for inhabitants of modest village. As a result of this human tragedy 2252 people were affected and 1043 people died. Therefore, efficient mercury remediation technologies evolvement is extremely urgent [6, 7].

Based on mercury properties, the physical adsorption between mercury and active adsorbents may not be effective. In majority of cases, the adsorbent's surface must be modified for chemical adsorption. It has been reported that several metals, such as palladium, platinum, rhodium, gold, zinc, aluminium, copper and silver are ready to form amalgam with mercury. Moreover, these metal amalgams formed with mercury have relatively low solubility, which implies negligible release of mercury after adsorption. Among those metals, it has been noted that silver has the lowest solubility, therefore, it was selected to modify adsorbent support and create more active sites [8, 9].

Activated carbon, carbon nanotube, zeolites, clays and mesoporous silicas are have been widely used for removal metal ions from aqueous system. However, because of their relatively high cost today especial attention has been devoted to finding inexpensive adsorbents [10].

Silica can be chosen as an efficiently adsorbent in water treatment processes because of its granular structure, water insolubility, chemical stability, high mechanical strength and its low costs. Alternative sources of silica such as rice husk and sugarcane bagasse have been used to obtain amorphous silica by costly templates, surfactants and use of acid washing under high temperature and atmospheric and thermal treatment methods [11]. For instance, RHA with 87.5 % silica content prepared by directly calcination of RH at 650 °C for 2 hours was used to synthesize poly inorganic silica with Fe and Al ions, which are more favorable in removal of heavy metals from wastewater [12, 13].

Different optimization approaches have been used to improve the adsorption capacity of the mesoporous silica. Katok et al. [14] have reported synthesis of composite materials by immobilization of silver nanoparticles on the silica surface functionalized with hydride groups. They were examined potential application of hydride silica composites as adsorbents for mercury from aqueous systems. These novel adsorbents demonstrate

high reactivity, pH sensitivity, capacity and can be effective candidate materials for removal mercury ions.

The method of silver nanoparticle immobilization on the surface of modified silica, which used in present work, has a list of significant advantages over other techniques. At first, it is economically feasible since it requires the minimum expense of the silver nitrate solution as a starting material. Secondly, silica can be synthesized using rice husk as a raw material [15]. Besides, it is anticipated that the synthesis of 'chemically pure' NPs results in hyperstoichiometry phenomena by which more efficient toxic metal remediation from water can be performed.

According to Katok et al. mercury ions in solution interact with silver metal (Ag^0) at a Ag:Hg stoichiometric ratio of 2:1 resulting in zero valent mercury [15]:

$$2Ag + Hg^{2+} \rightarrow 2Ag^+ + Hg \qquad (1)$$

Based on this stoichiometric ratio Katok et al. [15] described a hyperstoichiometric effect, according to which the Ag:Hg ratio changes depending on the Ag NPs size reaching 2:2.25. This ratio was taken from the quantity of Hg^{2+} reduced from solution with that of Ag^+ oxidized into solution. However, this is only part of the overall mechanism as redox is followed by amalgamation. The Hg^{2+} reduction and amalgamation were observed by Henglein and Brancewicz [16] and Henglein [17] who suggested the following reaction mechanism between Hg^{2+} and Ag NPs:

$$Ag_n + Hg^{2+} \rightarrow Ag_{(n-2)}Hg + 2Ag^+ \qquad (2)$$
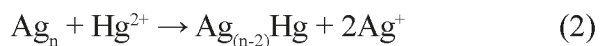
Harika et al. [18] studied the amalgamation reaction by ultrasonically reacting liquid mercury with an aqueous solution of silver nitrate. While the formation and role of silver nanoparticles is not discussed the authors observed schachnerite and moschellandsbergite and mixed phases with molar ratios of Ag:Hg from 2:1.33 up to 2:4. For instance, assuming the 2:1 ratio in the redox reaction and the formation of moschellandsbergite the overall reaction is:

$$8Ag + 3Hg^{2+} \rightarrow 6Ag^+ + Ag_2Hg_3 \qquad (3)$$
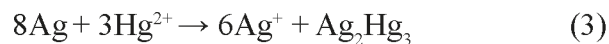
In the case of schachnerite:

$$2.9Ag + 0.9Hg^{2+} \rightarrow 1.8Ag^+ + Ag_{1.1}Hg_{0.9} \qquad (4)$$

Thus, the overall stoichiometric ratio could be 2:0.75, 2:0.62 depending on the formed amalgam.

Thus, present research work explored the preparation and characterization of new effectiveness inexpensive adsorbent prepared from agricultural wastes, namely rice husk silica to remove aqueous mercury ions from water specimens. The use of silica as an adsorbent not only solve the problem of potential human health risk and ecological disturbances related with toxic heavy metals but also will expand the feasibility of turning agricultural byproduct in to a valuable resource.

Materials and methods

Materials and chemicals. Triethoxysilane, glacial acetic acid, silver nitrate, mercury chloride were purchased from Sigma Aldrich and used without further purification. Rice was used as the main raw material for synthesizing silica by physical and chemical treatment methods. The mercury nitrate solution and microbiological samples collected on the Balkyldak Lake-reservoir were used in adsorption experiments.

Characterizations. Fourier Transform Infrared Spectroscopy (FTIR) was performed using Agilent technologies, Cary 600 series FTIR spectrometer in transmission (T) mode at mid IR, wavenumbers range 500-4000 cm^{-1} to conduct IR measurements. Band intensities can be also expressed in absorbance mode, in which same results are expected. The powder was then dispersed in a matrix of potassium bromide (KBr) in the ratio of ~1:10. The absorption coefficient of KBr is far less than 400 cm^{-1}, therefore no absorption peak of KBr appeared in the range of measurement.

Physical parameters of nitrogen adsorption/desorption for the Barret-Joyner-Halenda average pore diameter (D_{BJH}), the Brunauer-Emmett-Teller surface area (S_{BET}) and the total pore volumes (V_{total}) was obtained by Autosorb-iQ Automated

Gas Sorption Analyzer. Thermal characteristics of initial and modified samples of silica were measured by thermogravimetric analysis using TG/DSA 6000 instument (Perkin Elmer).

The removal of mercury ions from aqueous solution analyzed by RA-915M Mercury Analyzer with pyrolysis attachment (PYRO-915$^+$).

Synthesis of silica by physical-chemical treatment. The samples of rice husks were previously washed with water for the purification of the composition from foreign substances. Then the initial raw materials were dried in the laboratory drying oven at the temperature of 90 °C for 2 hours (for complete evaporation of the water in the composition). All prepared samples (50 g) were calcinated at 600 °C for 4 hours in a muffle furnace (AAF series, Carbolite) to produce white rice husk ash (WRHA). After the end of the process, all organic compounds in the rice husk are burned completely and eventually the ash of white rice husks is formed. Subsequently the WRHA was mixed with 100 ml of 2M NaOH at 90 °C at continuous vigorous stirring for 2 hours in order to extract the solid silica into water soluble sodium silicate. The water soluble sodium silicate solution was filtered via the vacuum pump to remove insoluble residues. After filtration, the water soluble sodium silicate solution (the filtrate) converted into insoluble silicic acid by reaction with concentrated HCl for 30 minutes, under continuous stirring.

Modification surface of rice husk silica samples with silicon hydride groups

Batch (3 g) of the silica oxide was added into a round bottom flask equipped with a reflux condenser. The flask was placed in a water bath with constant temperature (90 °C) and solution of modifier (0.4 ml triethoxysilane (TES, Sigma Aldrich, 390143, 95%) in 60 ml of the glacial acetic acid) was added under continuous stirring. After 2 h of reaction, the mixture was cooled to room temperature and filtered. Obtained solid was dried at 90 °C. Resulting modified silica samples were used for reaction of the silver nanoparticles formation.

Formation of Ag nanoparticles on the surface of silica

Silver nanoparticles formation on silica surface was as follows: 5 samples of modified silica (1.1 g. each) were immersed into silver nitrate (10 mmol·L^{-1}) aqueous solution at ambient temperature with different volume (5.5, 11, 22, 33, 44 ml) of silver nitrate; all experiments were carried out in the light shielded conditions to prevent the light degradation of the silver nitrate. Silver nanoparticles are formed on the surface of silica through the chemical reduction of silver ions into zero-valence state as result of reaction with silicon-hydride groups on the silica surface (Table 1). The obtained samples were filtered and dried for 12 h at 105 °C in the bench oven.

Mercury removal experiments

Silver nanoparticles deposited on the silica surface were tested in reactions with mercury chloride (HgCl$_2$), for each experiment 0.1 g of silver containing silica was placed in a conical flask and 10 ml of HgCl$_2$ (Sigma Aldrich, M6529, ≥99.5%) solution (100 mg/l) was added. The mixture was continuously stirred at ambient temperature for 1.5 hours. After reaction, the mixture centrifuged and solution analysed for mercury content. The real mercury containing solutions were sampled from the lake-reservoir Balkyldak and had an initial concentration 14836.6 ng/l. The residual mercury in the solution was analaysed by using the RA-915M Mercury Analyzer with pyrolyzer PYRO-915$^+$.

Results and discussion
Material characterization
Porosimetry. N$_2$ adsorption-desorption measurement were performed to characterize the textural properties of initial and TES-modified silica. Silica nanoparticles were obtained by thermal treatment of rice husk (RH) followed by separation of silica from the ashes of rice husks (RHA) code-named RHA-Si and subsequent modification by silane code-named RHA-Si/HSi and modified with silver nitrite RHA-Si/HSi/Ag.

Table 1 show the data of low-temperature nitrogen adsorption in accordance with the sample coding. Adsorption data for the silica samples were used to calculate the specific surface area, pore diameters and total pore volume by the BJH and BET method.

Table 1 – Porosimetry results

Sample	Surface area, (BET)	Surface area, (BJH)	V_{pore}, (BJH)	d_{pore}, (BJH)
	[m²/g]	[m²/g]	[cm³/g]	[nm]
RHA-Si	980	418	1.086	3.055
RHA-Si/HSi	285	166	0.895	4.723
RHA-Si/HSi/Ag	310	160	0.863	5.072

It follows from Table 1 that the RHA-Si/His and RHA-Si/HSi/Ag samples have a lower specific surface area (166, 160 m²/g) than the initial RHA-Si sample (418 m²/g), which is due to the modification of the sample by the silane, which partially covers the silica surface. This is confirmed by a decrease in the pore volume of the modified samples (0.895, 0.863 cm³/g) compared to the initial silica (1.086cm³/g).

The isotherms can be classified as type II Fig. 1b,c with macroporous and IV in Fig. 1a, according to IUPAC classification (Sing et al., 1985) [19] with an uptake in the low pressure region (p/$p_0 \leq 0.1$) characteristic of microporous materials. However, isotherm also shows a distinct hysteresis loop at intermediate to high relative pressures, which is characteristic of the presence of large micropores and mesopores (type IV). This is clearly shown on the graph of the pore size distribution in silica samples.
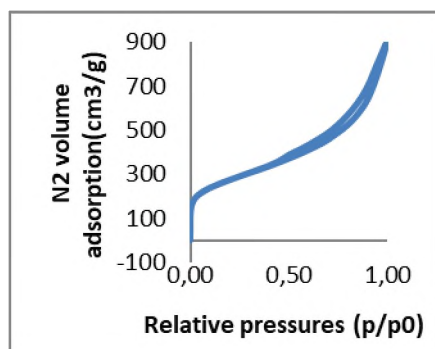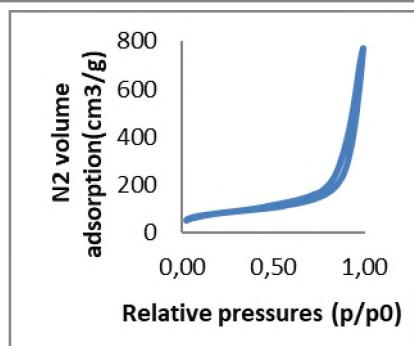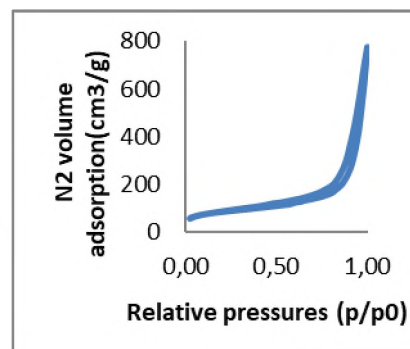

c

Figure 1 – Nitrogen adsorption-desorption isotherm of initial RHA-Si, RHA-Si/HSi, RHA-Si/HSi/Ag samples

Thermogravimetric analysis. The thermograph of the initial silica sample from the rice husks code-named RHA-Si is shown in Fig. 2.
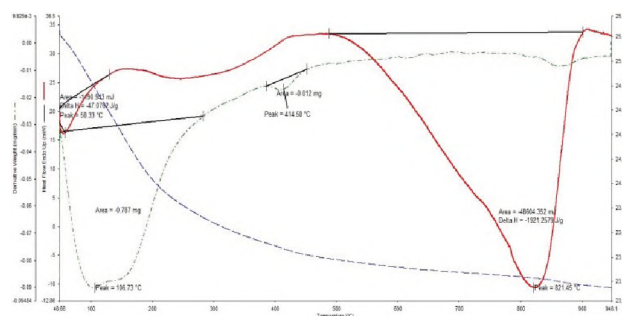

Figure 2 – Thermograph of RHA-Si sample

From the thermograph, it follows that when the sample was heated to 950 °C, a monotonic mass loss occurred throughout the entire period. In the first heating section up to 100 °C, the sample loses 2 % of the mass due to evaporation of water from the structure of the sample, which is evident from the energy consumption curve (red line). Further, there is a gradual loss of mass, but starting from 500 °C, a sharp consumption of energy begins and ends at 800 °C, which indicates that the unburned sodium salt is melted in the structure of the silica. At the end of the thermal analysis for a sample of silica from rice husk, it was found that the sample is heat-resistant and the weight loss is 9.1 %.
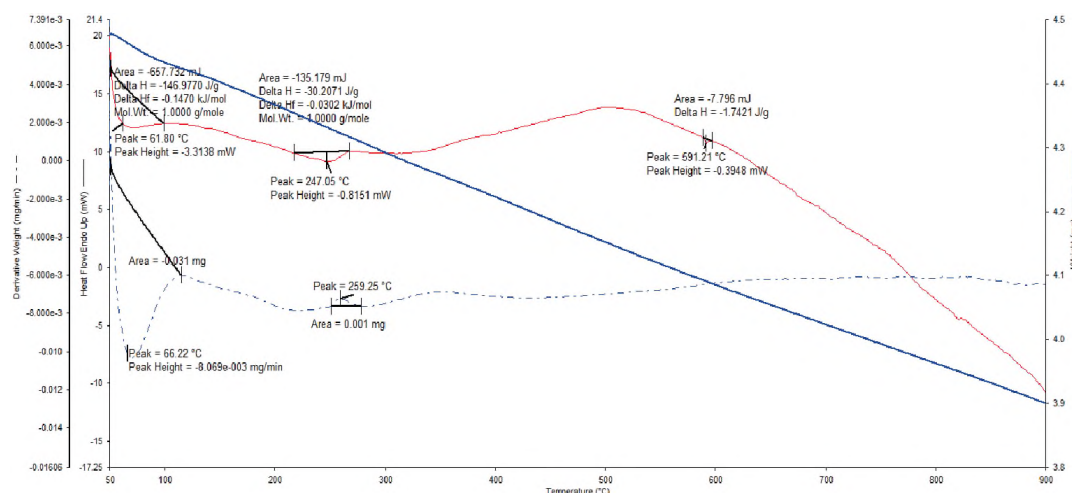

a

b

Figure 3 – Thermograph of RHA-Si/HSi sample

The data of the thermograph of the RHA-Si/HSi sample (Fig. 3) indicate a low mass loss (no more than 2.5 %) due to the evaporation of water at a temperature of 66 °C. Then there was a linear loss of mass without consumption or release of energy, but from 500 °C to 900 °C, an endothermic reaction occurred without a sudden jump in mass loss, which indicates an intrastructural change in the sample of the material. The total weight loss did not exceed 14 %.

FTIR results. The FT-IR spectra of (a) the unmodified silica, (b) the TES-modified silica and silver NPs decorated silica were shown in Fig. 3. Silica hydride groups anchored to the surface of silica particles possess weak reducing properties, which are sufficient for generating "chemically pure" zero-valent silver by the reduction of silver cation according to Equation (6).

$$\equiv SiH + Ag^+ + 2H_2O \rightarrow \equiv SiOH + Ag^0 + H_3O^+ + \tfrac{1}{2} H_2 \quad (6)$$
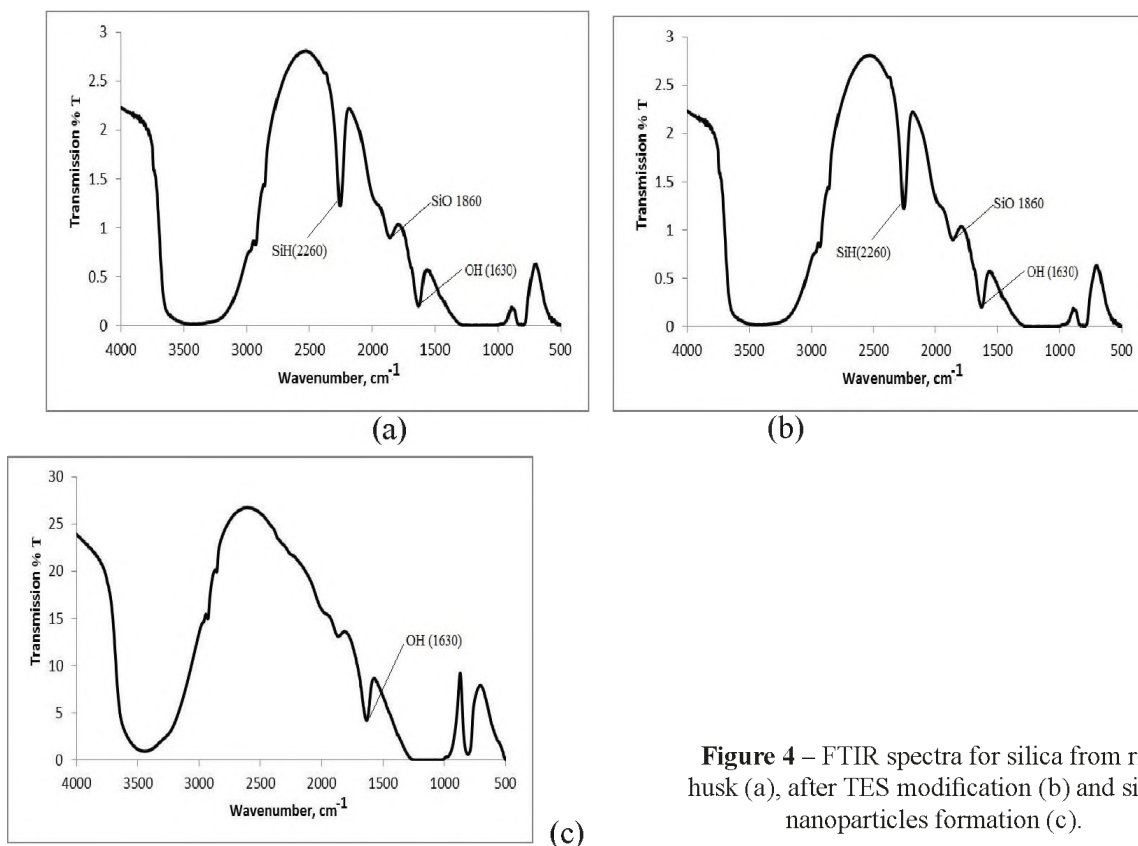

(a)

(b)

(c)

Figure 4 – FTIR spectra for silica from rice husk (a), after TES modification (b) and silver nanoparticles formation (c).

In the IR spectra of Silica, stretching vibrational bands of Si-O can be observed at 1860 cm^{-1} (Fig. 3a). After the modification of silica with triethoxysilane, the IR spectra contained an intense band with an absorption maximum at 2260 cm^{-1}. This band corresponds to Si–H bond stretching vibrations in surface chemical compounds (Fig. 3b). A broad absorption band at 3300-3800 cm^{-1} is evidence of the presence of adsorbed water and perturbed $\equiv$ SiOH groups in the surface layer. After modified silica was brought in contact with a solution of silver nitrate, and silver nanoparticles were reduced in the surface layer of silica matrices (Fig. 3c).

Mercury removal experiments

Synthetic solution. Different concentrations of silver nanoparticles on silica substrate were synthesized and calculated stoichiometric ratio of Hg^{II} to Ag^0: 0.005 mmol Ag/g SiO_2, 0.01 mmol Ag/g SiO_2, 0.02 mmol Ag/g SiO_2, 0.03 mmol Ag/g SiO_2, 0.04 mmol Ag/g SiO_2, 0.05 mmol Ag/g SiO_2, 0.1 mmol Ag/g SiO_2, 0.2 mmol Ag/g SiO_2, 0.3 mmol Ag/g SiO_2, 0.4 mmol Ag/g SiO_2.

All the obtained samples were assigned with the terms given in Table 2.

Table 2 – Different silver containing silica samples for interactions with mercury nitrate solution

Sample name of silver containing silica	Interactions with mercury nitrate solution
Ag NPs with content of 0.005 mmol Ag/g SiO_2	0.1 g of 0.005 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.01 mmol Ag/g SiO_2	0.1 g of 0.01 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.02 mmol Ag/g SiO_2	0.1 g of 0.02 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.03 mmol Ag/g SiO_2	0.1 g of 0.03 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.04 mmol Ag/g SiO_2	0.1 g of 0.04 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.05 mmol Ag/g SiO_2	0.1 g of 0.05 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.1 mmol Ag/g SiO_2	0.1 g of 0.1 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.2 mmol Ag/g SiO_2	0.1 g of 0.2 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.3 mmol Ag/g SiO_2	0.1 g of 0.3 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$
Ag NPs with content of 0.4 mmol Ag/g SiO_2	0.1 g of 0.4 mmol of Ag/g SiO_2 was mixed with 10 mL of 100mg/l of $HgCl_2$

The produced silver nanoparticles immobilized on silica support were tested on removal the mercury (II) ions from aqueous solution and calculated stoichiometric ratio of Hg^{II} to Ag^0 (Table 3).

Table 3 – Removal of Hg2+ from aqueous solution

Sample description	Stoichiometric ratio of Hg^{II} to Ag^0	Concentration of Hg^{2+} in water after sorption	Removal of Hg
		[ng/l]	[%]
0.005 mmol Ag/g SiO_2	7.4:1	21014.8	79
0.01 mmol Ag/g SiO_2	3.7:1	9741.3	90

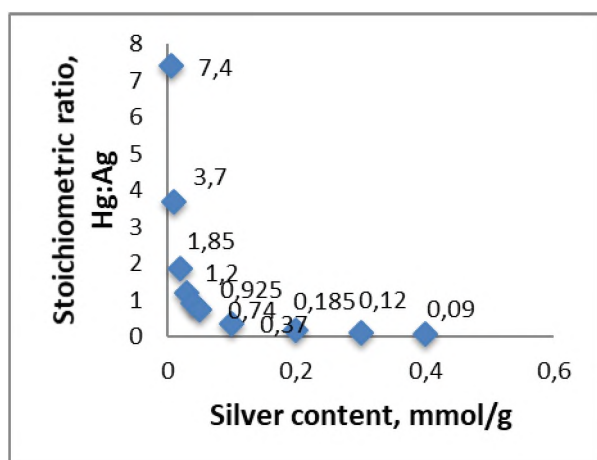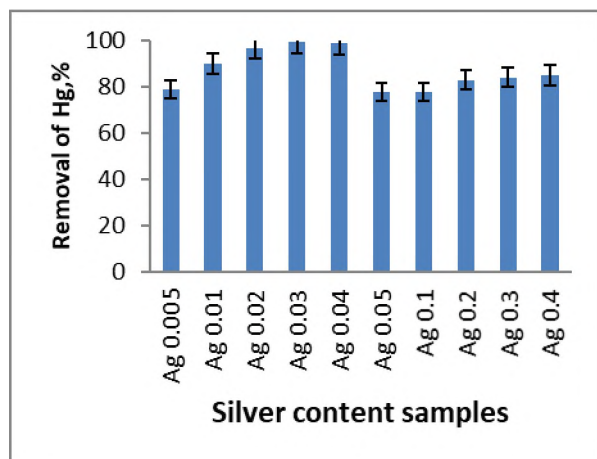| 0.02 mmol Ag/g SiO$_2$	1.85:1	2927.9	97
0.03 mmol Ag/g SiO$_2$	1.2:1	376.6	99.6
0.04 mmol Ag/g SiO$_2$	0.925:1	797.6	99.1
0.05 mmol Ag/g SiO$_2$	0.74:1	21431.5	78
0.1 mmol Ag/g SiO$_2$	0.37:1	20431.	78
0.2 mmol Ag/g SiO$_2$	0.185:1	17156.3	83
0.3 mmol Ag/g SiO$_2$	0.12:1	15557.3	84
0.4 mmol Ag/g SiO$_2$	0.09:1	14650.9	85

Figure 5 – Hg2+ removal in modular solution after sorption (left) and stoichiometric ratio Hg:Ag in reaction of mercury uptake (right).

Mercury adsorption onto hydride silica composites is a fast and efficient process, allowing the loading of up to 0.02, 0.03, 0.04 mmol of Ag/g SiO$_2$ adsorbent with a stoichiometric molar ratio 1.85:1, 1.2:1, 0.925:1 between Hg^{II} and Ag^0 on the silica surface.

Conclusions. 1. The adsorption of ionic mercury (II) from aqueous solution on functionalized hydride silicon materials was investigated.

2. The FTIR spectrum of a triethoxysilane surface-modified silica sample exhibits an intense absorption band at 2250 cm^{-1} that is typical of silicon hydride groups, in addition to the vibration bands observed for the native silica obtained from rice husk.

3. Experiments were carried out to investigate the effect of silver nitrate concentration, initial mercury concentration of the aqueous solution on mercury loading. The effectiveness of ionic mercury removal from an aqueous solution by adsorption onto silica with grafted silicon hydride groups occurs mainly by a redox mechanism: oxidation of $\equiv$SiH groups and reduction of Hg^{II} ions.

4. Mercury adsorption onto hydride silica composites is a fast and efficient process, allowing the loading of up to 0.2, 0.3, 0.4 mmol of Ag/g SiO$_2$ adsorbent with a stoichiometric molar ratio 0.185:1, 0.12:1, 0.09:1 between Hg^{II} and Ag^0 on the silica surface.

REFERENCES

1 *Ganzagh, M.A.A., Yousefpour, M., Taherian, Z.,* 2016. The removal of mercury (II) from water by Ag supported on nanomesoporous silica. Journal of Chemical Biology. 9, 127–142. https://doi.org/10.1007/s12154-016-0157-5.

2 *Arshadi, M., Mousavinia, F., Khalafi-Nezhad, A., Firouzabadi, H., Abbaspourrad. A.,* 2017. Adsorption of mercury ions from wastewater by a hyperbranched and multifunctionalized dendrimer modified mixed-oxides nanoparticles. Journal of Colloid and Interface Science. 505, 293–306. https://doi.org/10.1016/j.jcis.2017.05.052.

3 *Atwood, D.A., Zaman, M.K.,* 2006. Mercury removal from water. In: Atwood D.A. (Eds.) Recent Developments in Mercury Science. Structure and Bonding, Springer, Berlin, Heidelberg, pp. 163–182. https://doi.org/10.1007/430_013.

4 *Girginova, P.I., Daniel-da-Silva, A.L., Lopes, C.B., Figueira, P., Otero, M., Amaral, V.S., Pereira, E., Trindade, T.,* 2010. Silica coated magnetite particles for magnetic removal of Hg²⁺ from water. Journal of Colloid and Interface Science. 345, 234–240. https://doi.org/10.1016/j.jcis.2010.01.087.

5 *Ullrich, S.M., Ilyushchenko, M.A., Kamberov, I.M., Tanton. T.W.,* 2007. Mercury contamination in the vicinity of a derelict chlor-alkali plant. Part I: sediment and water contamination of Lake Balkyldak and the River Irtysh. Science of the Total Environment. 381, 1–16. https://doi.org/10.1016/j.scitotenv.2007.02.033.

6 *Schroeder, W.H., Munthe, J., Lindqvist, O.,* 1989. Cycling of mercury between water, air, and soil compartments of the environment. Water, Air, and Soil Pollution, pp. 337–347. https://doi.org/10.1007/BF00283335.

7 *Wang, Q., Kim, D., Dionysiou, D.D., Sorial, G.A., Timberlake, D.,* 2004. Sources and remediation for mercury contamination in aquatic systems—a literature review. Environmental Pollution. 131, 323–336. https://doi.org/10.1016/j.envpol.2004.01.010.

8 *Bootharaju, M.S., Pradeep, T.,* 2010. Uptake of toxic metal ions from water by naked and monolayer protected silver nanoparticles: An X-ray photoelectron spectroscopic investigation. The Journal of Physical Chemistry C. 114, 8328–8336. https://doi.org/10.1021/jp101988h.

9 *Khunphonoi, R., Khamdahsag, P., Chiarakorn, S., Grisdanurak, N., Paerungruang, A., Predapitakkun, S.,* 2015. Enhancement of elemental mercury adsorption by silver supported material. Journal of Environmental Sciences. 32, 207–216. https://doi.org/10.1016/j.jes.2015.01.008.

10 *Yu, Y., Addai-Mensah, J., Losic. D.,* 2012. Functionalized diatom silica microparticles for removal of mercury ions. Science and Technology of Advanced Materials. 13, 1–11. https://doi.org/10.1088/1468-6996/13/1/015008.

11 *Kumar, S., Sangwan, P., Dhankhar, R., Mor, V., Bidra, S.,* 2013. Utilization of Rice Husk and Their Ash: A Review. Research Journal of Chemical and Environmental Sciences. 1, 126–129. Available Online http://www.aelsindia.com.

12 *Abo-El-Enein, S.A., Eissa, M.A., Diafullah, A.A., Rizk, M.A., Mohamed, F.M.,* 2009. Removal of some heavy metals ions from wastewater by copolymer of iron and aluminum impregnated with active silica derived from rice husk ash. Journal of Hazardous Materials. 172, 574–579. https://doi.org/10.1016/j.jhazmat.2009.07.036.

13 *Sun, L., Gong, K.,* 2001. Silicon-based materials from rice husks and their applications. Industrial & Engineering Chemistry Research. 40, 5861–5871. https://doi.org/10.1021/ie010284b.

14 *Katok, K.V., Whitby, R.L.D., Fayon, F., Bonnamy, S., Mikhalovsky, S.V., Cundy, A.B.,* 2013. Synthesis and application of hydride silica composites for rapid and facile removal of aqueous mercury. ChemPhysChem, 14, 4126–4133. https://doi.org/10.1002/cphc.201300832.

15 *Katok, K.V., Whitby, R.L.D., Fukuda, T., Maekawa, T., Bezverkhyy, I., Mikhalovsky, S.V., Cundy, A.B.,* 2012. Hyperstoichiometric interaction between silver and mercury at the nanoscale. Angewandte Chemie International Edition. 51, 2632–2635. https://doi.org/10.1002/anie.201106776.

16 *Henglein, A., Brancewicz, C.,* 1997. Absorption spectra and reactions of colloidal bimetallic nanoparticles containing mercury. Chemistry of Materials. 9, 2164–2167. https://doi.org/10.1021/cm970258x.

17 *Henglein, A.,* 1998. Colloidal silver nanoparticles: Photochemical preparation and interaction with O2, CCl4, and some metal ions. Chemistry of Materials. 10, 444–450. https://doi.org/10.1021/cm970613j.

18 *Harika, V.K., Kumar, V.B., Gedanken, A.,* 2018. One-pot sonochemical synthesis of Hg-Ag alloy microspheres from liquid mercury. Ultrasonics Sonochemistry. 40, 157–165. https://doi.org/10.1016/j.ultsonch.2017.07.008.

19 *Sing, K.S.W.,* 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). IUPAC Commission on Colloid and Surface Chemistry Including Catalysis. Pure and Applied Chemistry. 57, 603–619. https://doi.org/10.1351/pac198557040603.

СУДАҒЫ СЫНАП ИОНДАРЫН ТАЗАРТУҒА АРНАЛҒАН ЖАҢА АДСОРБЕНТ РЕТІНДЕ БИОЛО-ГИЯЛЫҚ КӨЗДЕРДЕН АЛЫНҒАН КҮМІС ЖӘНЕ КРЕМНИЙ ДИОКСИДІ НЕГІЗІНДЕГІ КОМПОЗИТТІК МАТЕРИАЛДАР

Түйіндеме. Бұл зерттеуде судан сулы сынап иондарын кетіру үшін шикізат ретінде күріштен алынған кремний диоксиді, күміс нанобөлшектері және триэтоксисилан қолданылатын жаңа композициялық ад-сорбенттің синтезі ұсынылған. Жаңа композициялық материал күріш қабығы негізіндегі кремнеземнің бетін силан топтарымен модификациялау және одан әрі күміс нанобөлшектермен безендіру арқылы синтезделді. Сипаттама Фурье түрлендіру инфрақызыл (FT-IR) спектрлік талдау, N2 адсорбциялық-де-сорбциялық (Брунауэр-Эммет-Теллер) және термиялық гравиметриялық талдау (TGA) арқылы жүзе-ге асырылды. Қазақстандағы Балқылдақ көл-су қоймасынан алынған судың құрамында синтетикалық және нақты сынап бар. Нәтижелер композиттің сынапқа жақындығы жоғары екенін және жою механизмі күміс пен сынап арасындағы амальгация реакциясымен жүретін адсорбция екенін көрсетті.

Түйін сөздер: Адсорбция, күміс нанобөлшектері, күріш қабығы кремний диоксиді, кремний/Ag компо-зиттері, сулы сынап иондары

Графикалық реферат
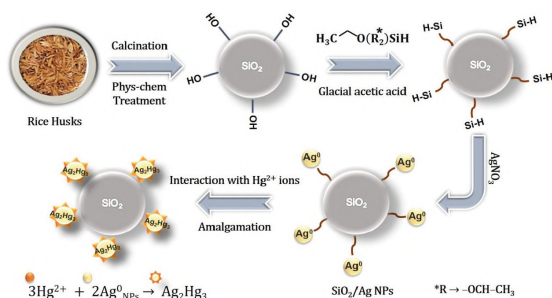
Сурет 0 – Композиттік материалдарды дайындаудың тәжі-рибелік процедурасының схемалық суреті.

SiO$_2$/AgNPs негізіндегі күріш қабығына Hg2+ иондарының адсорбциялануының ұсынылған механизмі 0-суретте көр-сетілген.

КОМПОЗИТНЫЕ МАТЕРИАЛЫ НА ОСНОВЕ ДИОКСИДА КРЕМНИЯ И СЕРЕБРА ИЗ БИОЛОГИ-ЧЕСКИХ ИСТОЧНИКОВ В КАЧЕСТВЕ НОВОГО АДСОРБЕНТА ДЛЯ УДАЛЕНИЯ ИОНОВ РТУТИ ИЗ ВОДЫ

Аннотация. В данном исследовании представлен синтез нового композитного адсорбента с использо-ванием диоксида кремния из риса, наночастиц серебра и триэтоксисилана в качестве сырья для удале-ния водных ионов ртути из воды. Новый композиционный материал был синтезирован путем модифи-кации поверхности кремнезема на основе рисовой шелухи силановыми группами и дальнейшего деко-рирования наночастицами серебра. Определение характеристик проводили с помощью инфракрасного спектрального анализа с преобразованием Фурье (FT-IR), адсорбции-десорбции N2 (Брунауэра-Эммет-та-Теллера) и термогравиметрического анализа (ТГА). Были протестированы образцы синтетической и настоящей ртутьсодержащей воды из озера-водохранилища Балкылдак, Казахстан. Результаты по-казали, что сродство композита к ртути велико, а механизм удаления - адсорбция, сопровождаемая реакцией амальгамирования между серебром и ртутью.

Ключевые слова: адсорбция, наночастицы серебра, кремнезем рисовой шелухи, композиты кремне-зем / Ag, водные ионы ртути.
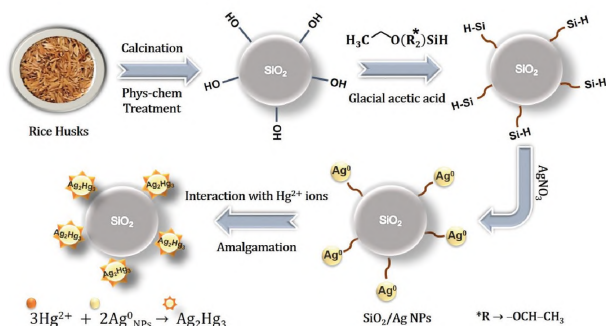
Графическая абстракция

Рисунок 0 - Схематическое изображение экспери-ментальной процедуры изготовления композицион-ных материалов.

Предлагаемый механизм адсорбции ионов Hg2 + на композиционных материалах SiO$_2$ / AgNPs на ос-нове рисовой шелухи показан на рис.0.

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